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Neutral and cationic yttrium alkyl complexes with linked 1,4,7-triazacyclononane-amide monoanionic ancillary ligands: synthesis and catalytic ethene polymerisation†‡

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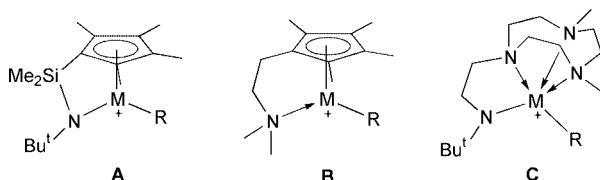
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Yttrium dialkyl complexes $[N,N'-R_2\text{-tacn-}N''\text{-(CH}_2)_2\text{NBu}^t]\text{-Y(CH}_2\text{SiMe}_3)_2$ ($R = \text{Me, Pr}^i$; tacn = 1,4,7-triazacyclononane) were prepared; when activated with $[\text{PhNMe}_2\text{H}]\text{-[B(C}_6\text{F}_5)_4]$ these complexes form cationic alkyl species that are active ethene polymerisation catalysts.

Cationic group 4 metal alkyl species with linked dianionic cyclopentadienyl-amide ancillary ligands, such as $[\text{C}_5\text{Me}_4\text{Si-Me}_2\text{NBu}^t]\text{M(alkyl)}^+ \text{A}$ ($M = \text{Ti, Zr}$), are highly efficient

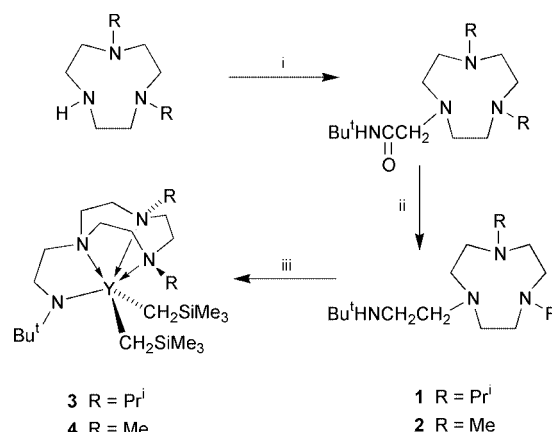


catalysts for the polymerisation of alkenes.¹ The isoelectronic group 3 metal alkyl complexes with these ligands are neutral, and much less effective in alkene polymerisation.² One approach that might allow the generation of cationic group 3 metal alkyl species is to replace either one of the monoanionic moieties of the ancillary ligand (amide or cyclopentadienyl) by a neutral functionality. A recent patent showed that replacement of the amide group by an amine donor can lead to $[\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{NMe}_2]\text{M(alkyl)}^+ \text{B}$, ($M = \text{Sc}$) species that are active in catalytic alkene polymerisation.³ We have designed a ligand in which an amido functionality is attached to a substituted 1,4,7-triazacyclononane (tacn) group, and that allowed us to generate cationic tacn-amide group 3 metal alkyl complexes of type C. These species were found to be highly active in the catalytic polymerisation of ethene.

1,4,7-Triazacyclononane ligands have been successfully used as 6-electron *fac*-tridentate ligands on a wide range of transition metals, and various neutral and anionic tacn derivatives have appeared in the literature recently.⁴ The new tacn-amine derivatives $N,N'-R_2\text{-tacn-}N''\text{-(CH}_2)_2\text{NBu}^t\text{H}$ ($R = \text{Pr}^i$, **1**; $R = \text{Me}$, **2**) were prepared in two steps from the known corresponding N,N' -dialkyl-1,4,7-triazacyclononanes⁵ (Scheme 1). Reaction of these N,N' -dialkyltriazacyclononanes with *N*-tert-butylchloroacetamide in refluxing acetonitrile, with a catalytic amount of NaI, yielded the corresponding *N*-tert-butyl-(4,7-dialkyl-1,4,7-triazacyclonon-1-yl)acetamides. These were then reduced with LiAlH_4 in refluxing diglyme and purified, after hydrolysis and acid–base extraction, by Kugelrohr distillation (**2**) or column chromatography (**1**).

Reaction of the amine **1** with the yttrium trialkyl $\text{Y(CH}_2\text{SiMe}_3)_3(\text{thf})_6$ in C_6D_6 results in formation of SiMe_4 , free thf, and the yttrium dialkyl complex $[N,N'\text{-Pr}_2\text{-tacn-}N''\text{-}$

$(\text{CH}_2\text{CH}_2)\text{NBu}^t]\text{Y(CH}_2\text{SiMe}_3)_2$ **3**, (Scheme 1), as seen by NMR spectroscopy. The same reaction in pentane solvent (0.5 mmol scale), followed by crystallization, yielded analytically pure, white crystalline **3**. The isolated yield (28%) was rather modest, mainly due the high solubility of the product. An X-ray structure determination of **3** confirmed its identification as a monomeric, thf-free yttrium dialkyl (Fig. 1). As expected, the three nitrogens of the tacn moiety are bound in *fac* arrangement to the metal centre. There is considerable asymmetry in the structure of the complex, as seen *e.g.* in the angle N(1)-Y-C(19) $113.8(2)^\circ$ vs. N(1)-Y-C(23) $95.9(2)^\circ$, and the groups are



Scheme 1 Reagents and conditions: i, *N*-tert-butylchloroacetamide, MeCN, cat. NaI, reflux, 1 h; ii, LiAlH_4 , diglyme, reflux, 3 h (**2**) or 100 h (**1**), followed by hydrolysis and acid–base extraction; iii, $\text{Y(CH}_2\text{SiMe}_3)_3(\text{thf})_2$, pentane, 14 h, 20°C .

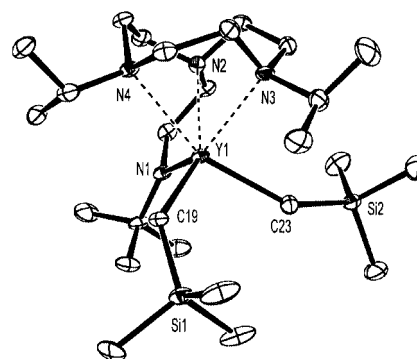


Fig. 1 Molecular structure of **3** (hydrogen atoms omitted for clarity, unlabeled atoms are carbon, thermal ellipsoids drawn at 30% probability level). Selected interatomic distances (Å) and angles ($^\circ$): Y-N(1) 2.231(5), Y-N(2) 2.541(5), Y-N(3) 2.618(5), Y-N(4) 2.740(5), Y-C(19) 2.476(5), Y-C(23) 2.421(7); C(19)-Y-C(23) $101.1(2)$, N(1)-Y-N(2) $72.4(2)$, N(2)-Y-N(3) $68.8(2)$, N(2)-Y-N(4) $65.5(2)$, N(3)-Y-N(4) $68.9(2)$, N(3)-Y-C(23) $86.7(2)$, N(4)-Y-C(19) $82.7(2)$, Y-C(19)-Si(1) $134.2(3)$, Y-C(23)-Si(2) $145.4(4)$.

† Electronic supplementary information (ESI) available: experimental, spectroscopic and polymerization details. See <http://www.rsc.org/suppdata/cc/b1/b101012n/>

‡ Netherlands Institute for Catalysis Research (NIOK) publication no. RUG 01-4-01.

Table 1 Catalytic ethene polymerisation with **3** and **4** in conjunction with [PhNMe₂H][B(C₆F₅)₄] activator^a

Dialkyl	<i>T</i> /°C	PE yield/g	Productivity/ 10 ³ kg(PE) mol(Y) ^{−1} h ^{−1} bar ^{−1}	10 ^{−3} <i>M</i> _w	<i>M</i> _w / <i>M</i> _n
4	30	5.62	0.70	471	4.0
4	50	9.40	1.18	325	4.9
4	80	14.30	1.79	98	6.0
3^b	30	11.95	0.96	— ^c	— ^c

^a Conditions: toluene solvent (150 ml), 10 μmol Y dialkyl complex, 10 μmol activator, 5 bar ethene pressure, 10 min run time. ^b 15 min run time. ^c Not determined.

arranged in such a way as to prevent the eclipsing of the ligand Prⁱ and Y-alkyl groups. The Y–N distances for the tacn nitrogens span a considerable range, the shortest being the distance to the bridgehead nitrogen Y–N(2), 2.541(5) Å, and the longest the Y–N(4) distance, 2.740(5) Å, N(4) being practically *trans* to C(23). This asymmetry appears to be retained in solution, as the ambient temperature ¹H and ¹³C NMR spectra show resonances consistent with an asymmetric species (e.g. four resonances for the diastereotopic CH₂SiMe₃ methylene protons).⁷ The alkyl methylene carbon resonances are found at δ 33.7 and 31.0, with rather large ¹J_{YC} coupling constants (ca. 38 Hz) and relatively small ¹J_{CH} coupling constants of 95 Hz.

Reaction of the amine **2** with Y(CH₂SiMe₃)₃(thf)₂ in pentane yielded the corresponding dialkyl complex [N,N'-Me₂-tacn-N''-(CH₂CH₂)NBuⁱ]Y(CH₂SiMe₃)₂ **4**, analytically pure in 86% isolated yield. The smaller size of the alkyl substituents makes the complex more fluxional, as the room temperature ¹H NMR spectrum of **4** shows broad resonances consistent with a species with an average C_s symmetry. Cooling a toluene-*d*₈ solution of **4** to −60 °C slows down this dynamic process, revealing spectra with four Y-alkyl methylene and two Y–C resonances, again consistent with an asymmetric ground state structure.⁸

The dialkyl complex **4** reacts cleanly with the Brønsted acid [PhNMe₂H][B(C₆F₅)₄]⁹ in C₆D₅Br solvent to give SiMe₄, free PhNMe₂, and an ionic species formulated as {[N,N'-Me₂-tacn-N''-(CH₂CH₂)NBuⁱ]Y(CH₂SiMe₃)₂}[B(C₆F₅)₄][−] **6**.¹⁰ The ¹H NMR spectrum shows a single resonance at δ −1.06 for the YCH₂ group (*J*_{YH} not resolved), and the ¹³C NMR YCH₂ resonance at δ 37.0 (*J*_{YC} 40.7 Hz), shifted downfield and with a larger *J*_{YC} relative to the dialkyl **4**. The ionic species **6** is thermally relatively stable, and remains essentially unchanged over 1 h at ambient temperature in bromobenzene solution. In contrast, reaction of the dialkyl complex **3** with [PhNMe₂H][B(C₆F₅)₄] leads to rapid formation of propene and 2 equiv. of SiMe₄ (as seen by ¹H NMR spectroscopy), and an ill-defined yttrium species. Apparently, an Prⁱ substituent on the ancillary ligand is metallated on one of its methyl groups, followed by elimination of propene. When the reaction is performed in the presence of an excess of *d*₈-thf, the cationic alkyl species is trapped before ligand metallation occurs, giving a species formulated (based on its ¹H NMR characteristics) as {[N,N'-Prⁱ-tacn-N''-(CH₂CH₂)NBuⁱ]Y(CH₂SiMe₃)(*d*₈-thf)}⁺[B(C₆F₅)₄][−] (**5-d₈-thf**), with YCH₂ resonances at δ −1.29 and −1.35 (dd, ²*J*_{HH} 11.0 Hz, *J*_{YH} 3.0 Hz).¹¹

Ethylene homopolymerisation experiments (toluene solvent) showed that the dialkyls **3** and **4**, in combination with the Brønsted acid activator [PhNMe₂H][B(C₆F₅)₄], yield active ethene polymerisation catalysts, with observed productivities up to 1.79 × 10³ kg(PE) mol(Y)^{−1} h^{−1} bar^{−1}. Relatively short run times (10–15 min) were chosen to minimise inhomogeneity and mass transfer effects. Over the run period the catalysts show a modest (25–30%) decrease in ethene uptake rate. The results listed in Table 1 show that the productivity of the Me₂-tacn system is enhanced by increasing the reaction temperature, but that the polydispersity of the polyethene produced also increases substantially. One possible explanation for this is that the initial cationic alkyl catalyst is thermally transformed into another species that is also active in the polymerisation of

ethene, thus leading to bimodal product distributions. The polymerisation behaviour of this type of catalyst and its dependence on various parameters (ligand substitution pattern, activator species, etc.) is subject of further study.

In conclusion, we have prepared new yttrium dialkyl species with monoanionic tetradentate triazacyclononane-amide ancillary ligands. Reactions of these dialkyls with [PhNMe₂H][B(C₆F₅)₄] generate the ionic species **5-thf-d₈** and **6**, rare examples of spectroscopically characterised cationic group 3 metal alkyls.¹² These cationic alkyl species are active catalysts for the polymerisation of ethene.

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Notes and references

§ Crystallographic data for **3**: C₂₆H₆₁N₄Si₂Y, *M* = 574.87, triclinic, space group P $\bar{1}$, *a* = 9.815(1), *b* = 9.859(1), *c* = 17.291(1) Å, α = 95.60(1), β = 90.68(1), γ = 98.63(1)°, *U* = 1645.7(4) Å³, *T* = 130 K, *Z* = 2, *D*_c = 1.160 g cm^{−3}, μ = 18.6 cm^{−1}, Enraf-Nonius CAD4-F diffractometer, λ(Mo-Kα) = 0.71073 Å, 6433 unique reflections, final residuals *wR*(*F*²) = 0.1800, *R*(*F*) = 0.0731 for 3940 reflections with *F*_o ≥ 4σ(*F*_o) and 311 parameters. CCDC 157466. See <http://www.rsc.org/suppdata/cc/b1/b101012n/> for crystallographic data in .cif or other electronic format.

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- Selected NMR data for **3**: ¹H NMR (500 MHz, C₆D₆) δ −0.26 (dd, *J*_{HH} 10.5, *J*_{YH} 3.3 Hz, 1H, YCHH), −0.53 (dd, *J*_{HH} 10.8, *J*_{YH} 2.1 Hz, 1H, YCHH), −0.83 (dd, *J*_{HH} 10.8, *J*_{YH} 3.0 Hz, 1H, YCHH), −1.00 (dd, *J*_{HH} 10.8, *J*_{YH} 2.1 Hz, 1H, YCHH). ¹³C NMR (125.7 MHz, C₆D₆) δ 33.7 (dt, *J*_{YC} 36.9, *J*_{CH} 95.1 Hz, YCH₂), 31.0 (t, *J*_{YC} 38.7, *J*_{CH} 95.0 Hz, YCH₂).
- Selected NMR data for **4**: ¹H NMR (500 MHz, −60 °C, C₇D₈) δ −0.62 (d, *J*_{HH} 11.0 Hz, 1H, YCHH), −0.86 (d, *J*_{HH} 11.0 Hz, 1H, YCHH), −0.94 (d, *J*_{HH} 11.0 Hz, 1H, YCHH), −1.06 (d, *J*_{HH} 10.5 Hz, 1H, YCHH). The *J*_{YH} coupling on the YCH₂ protons is unresolved. ¹³C NMR (125.7 MHz, −60 °C, C₇D₈) δ 29.8 (dt, *J*_{YC} 35.4, *J*_{CH} 93.3 Hz, YCH₂), 28.5 (dt, *J*_{YC} 38.9, *J*_{CH} 97.3 Hz, YCH₂).
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- NMR data for the cation of **6**: ¹H NMR (500 MHz, −30 °C, C₆D₅Br) δ 2.58–2.22 (m, 16H, NCH₂), 2.18 (s, 6H, NMe), 1.09 (s, 9H, Buⁱ), 0.11 (s, 9H, CH₂SiMe₃), −1.06 (br, 2H, YCH₂). ¹³C{¹H} NMR (125.7 MHz, C₆D₅Br, −30 °C) δ 60.09 (NCH₂), 56.05 (NCH₂), 53.33 (CMe₃), 53.75 (NCH₂), 51.78 (NCH₂), 46.51 (NMe), 46.16 (NCH₂), 37.02 (d, *J*_{YC} 40.7 Hz, YCH₂), 30.17 (CMe₃), 4.31 (SiMe).¹²
- NMR data for the cation of **5-thf-d₈**: ¹H NMR (500 MHz, −30 °C, C₆D₅Br-thf-d₈) δ 3.48 (sept, *J*_{HH} 6.0 Hz, 1H, CHMe₂), 3.40 (t, *J*_{HH} 13.0 Hz, 1H, NCH₂), 2.79–2.75 (m, 2H, NCH₂), 2.68–2.59 (m, 3H, NCH₂), 2.55–2.48 (m, 2H, NCH₂), 2.42–2.29 (m, 3H, NCH₂), 2.25–2.17 (m, 3H, NCH₂), 1.27 (br, 1H, CHMe₂), 1.18 (d, *J*_{HH} 6.0 Hz, 6H, CHMe₂), 1.15 (s, 9H, Buⁱ), 0.84 (d, *J*_{HH} 5.5 Hz, 3H, CHMe₂), 0.80 (d, *J*_{HH} 5.5 Hz, 3H, CHMe₂), 0.09 (s, 9H, Me₃SiCH₂), −1.29 (dd, *J*_{HH} 11.0, *J*_{YH} 3.0 Hz, 1H, YCHH), −1.35 (dd, *J*_{HH} 11.0, *J*_{YH} 3.0 Hz, 1H, YCHH).
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